

## PRECURSOR SOLUTIONS FOR BIOLOGICALLY ACTIVE GLASS

### BACKGROUND OF THE INVENTION

This invention concerns precursors for biologically active glass in the form of a stable aqueous solution, spheroidal glass particles, supports coated with the precursors, supports coated with the glass, and methods for making the precursor solution, the coated support and the glass particles.

As pointed out by Hench in a review article entitled "Biomaterials" in *Science*, 208, 826 to 831 (1980), some 2 to 3 million artificial or prosthetic parts are implanted in individuals in the United States each year. These devices, made from a wide variety of materials, are useful, for example, in the eye, the ear, and the nervous system; in the heart, limbs, bladder, and blood vessels; and to repair and replace bones, ligaments, and teeth. In these uses they combat both the degenerative effects of aging and damage resulting from accidents.

A summary of the status of biomaterials and the problems associated with them has been presented by Hall in *J. Biomed. Mater. Res. Symposium*, No. 2 (Part 1), pages 1 to 4 (1971). The article stresses the importance of the interface between an implant and the body tissue of the host.

U.S. Pat. No. 4,171,544 discloses numerous biologically active glass compositions.

U.S. Pat. No. 4,103,002 discloses a method for coating an alumina ceramic surface with a biologically active glass. The patent points out that alumina ceramic surfaces are biologically inactive and that bone tissue will not bond to or grow on them.

U.S. Pat. No. 4,159,358 discloses a method for bonding a biologically active glass to a metal surface. In discussing the use of biologically active glasses as biomaterials, the patent states that it is impossible to construct sufficiently strong orthopedic or dental devices from them.

### SUMMARY OF THE INVENTION

This invention concerns an aqueous acid solution composition of precursors for biologically active glass. The aqueous acid solution of the invention comprises a combination of all the precursors necessary to give a finished product when the precursor composition is dried and fired. This invention is not limited to any particular precursors for any specific biologically active glass. On the contrary, any combination of precursors can be employed which will form a coating of biologically active glass on the support particles.

The term "biologically active glass" means that the glass can form in vivo bonds with bone, muscle and other body tissues. For the sake of brevity, the term "glass" is employed herein to refer to biologically active glass. The term "aqueous solution" means an aqueous acid solution, suspension or dispersion of glass precursors.

This invention also concerns compositions of support particles coated with the glass precursors and support particles coated with the glass formed by calcining the glass precursors. This invention also concerns spheroidal particles of biologically active glass made by spray-drying the glass precursors and firing the spray-dried particles. Also included within the scope of this invention are methods for making the solution compositions of glass precursors, for coating the support particles, for

drying and firing the precursor-coated supports to form glass-coated/fused support particles and for spray-drying the solution composition of glass precursors. The spheroidal particles are characterized by their generally spherical geometry and relatively smooth surfaces. Glass particles of this invention can be easily distinguished from the rough-edged, substantially non-spherical glass particles of the prior art by microscopic examination.

### DETAILS OF THE INVENTION

#### The Biologically Active Glass

The following patents disclose a number of biologically active glasses that can be made by the process of this invention: U.S. Pat. Nos. 4,159,358, 4,103,002 and 4,171,544. In general, this invention encompasses any glass whose components can be prepared in a stable aqueous solution. By "stable" is meant that there is no substantial amount of precipitation in a period of one hour.

A typical composition range for a subclass of contemplated glass, which according to the convention used in glass chemistry is given in terms of oxides and fluoride, is as follows:

Component	Weight Percent
SiO <sub>2</sub>	40 to 62
Na <sub>2</sub> O	10 to 32
CaO	10 to 32
CaF <sub>2</sub>	0 to 18
P <sub>2</sub> O <sub>5</sub>	0.1 to 12
B <sub>2</sub> O <sub>3</sub>	0 to 20,

wherein the sum of Na<sub>2</sub>O and CaO is at least about 30 weight percent. Of the listed components, CaF<sub>2</sub> is not water-soluble. Consequently, an aqueous solution of glass precursors that comprises CaF<sub>2</sub> as a component is treated to suspend the CaF<sub>2</sub>. One method of treatment comprises adding a solution of fluoride ions (via NaF or NH<sub>4</sub>F) to a solution of Ca<sup>++</sup> with vigorous mixing. Preferred glasses of this type contain about 0.5 to 6 weight percent of P<sub>2</sub>O<sub>5</sub>.

Another subclass of contemplated glasses comprises those that contain boron. A typical boron-containing glass contains: 40 wt percent of SiO<sub>2</sub>, 5 wt percent of B<sub>2</sub>O<sub>3</sub>, 6 wt percent of P<sub>2</sub>O<sub>5</sub>, 24.5 wt percent of CaO, and 24.5 wt percent of Na<sub>2</sub>O.

#### The Support

Contemplated materials that can be employed as supports for the glass include high melting mineral oxides, ceramics, and the like. In fact, any material can be employed that will not adversely react with the glass, glass precursors or body parts with which said material may come in contact. It will be understood, of course, that said material should be relatively tough and stable at the elevated temperatures employed to fire the glass.

Contemplated support materials include alumina, silica, carbon, silica-aluminas, titania, clays, calcium silicate, feldspar, zinc oxide and the like, including any metal that the body will accept. Preferred supports are alumina, silica, titania, and mixtures and compositions thereof. The size and concentration of the support particles will vary in accordance with the particular device being fabricated, its intended use, and the desired composition of the particles. Contemplated particle sizes range up to about 1 mm or more in diameter.